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Noboru UENISHI, et al.	:	Confirmation Number: 5407
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For: ELECTRICAL CONTACT AND ELECTRICAL EQUIPMENT INCLUDING THE SAME

**SUBMISSION OF CERTIFIED TRANSLATION OF PRIORITY DOCUMENT**

Mail Stop Amendment  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

This application is entitled to have the benefit of an earlier filing date of July 18, 2003, based on Japanese patent application No. 2003-199389, pursuant to 35 U.S.C. §119. Applicants submit a certified English language translation of Japanese Application No. 2003-199389, filed July 18, 2003.

Respectfully submitted,

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I, Kumiko Kawai of Tranomon East Building, 7-13, Nishi-Shimbashi 1-chome, Minato-ku, Tokyo 105-8408, Japan, hereby declare that I am conversant with the Japanese and the English languages and that I am the translator of the document attached and certify that to the best of my knowledge and belief the following is a true and correct English translation of the specification contained in the Japanese Patent Application No. 2003-199389.

Signed, September 21, 2007

A handwritten signature in black ink, appearing to be 'Kumiko Kawai', written over a horizontal line.

Kumiko Kawai

Patent Department



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[Title of the Invention]   ELECTRICAL CONTACT

[Claims]

[Claim 1]   An electrical contact comprising an Ag alloy containing Sn in an amount of from 1 to 9% by weight and Cd as an impurity in an amount of less than 1% by weight and having an average hardness of 150 mHv or more on the microvickers scale defined in JIS at least on the surface thereof.

[Claim 2]   The electrical contact as defined in Claim 1, wherein there is provided a two-layer structure comprising a surface layer having an average surface hardness of 150 mHv or more and an inner layer having a lower hardness than that of the surface layer and the thickness of the surface layer is 10  $\mu$ m or more.

[Claim 3]   The electrical contact as defined in Claim 2, wherein the content of Sn in the surface layer is equal to or more than that of the inner layer.

[Claim 4]   The electrical contact as defined in any one of Claims 1 to 3, comprising at least one element selected from the group consisting of In, Sb, Ca, Bi, Ni, Co, Zn, Te, Cr and Pb incorporated therein as additives other than Sn.

[Claim 5]   The electrical contact as defined in any one of Claims 2 to 4, wherein the average hardness of the surface layer is 160 mHv or more.

[Claim 6]   The electrical contact as defined in Claim 5,

wherein the average hardness of the surface layer is 180 mHv or more.

[Claim 7] The electrical contact as defined in Claim 6, wherein the average hardness of the surface layer is 190 mHv or more.

[Claim 8] The electrical contact as defined in Claim 7, wherein the average hardness of the surface layer is 220 mHv or more.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates mainly to an electrical contact useful for wiring circuit breaker, no fuse breaker, circuit-breaker, safety breaker, distribution panel breaker (hereinafter collectively referred simply to as "breaker"), relay or electromagnetic switch and breaker comprising same.

[0002]

[Related Art]

As the material constituting a breaker or an electromagnetic switch having a heavy load, e.g., electromagnetic switch having a rated load of 35 A or more there has been heretofore used an Ag alloy having an oxide of Cd, Sn or In dispersed therein. In particular, an Ag alloy having Cd or Sn oxide dispersed therein is optimum for this kind of an electrical contact and has been widely used for

breaker or electromagnetic switch.

[0003]

However, Cd compounds are disadvantageous in toxicity. It has thus been desired to develop substitute electrical contact materials. In recent years, it has been keenly desired to develop a contact material made of Ag alloy having Sn or In oxide dispersed therein, i.e., so-called Cd-free Ag alloy. Many materials have been developed and used in many electrical appliances.

[0004]

The electrical contact made of a Cd-free Ag alloy is suitable for relatively light load electrical apparatus on which temperature properties are considered important and light load switch on which contact resistance is considered severe. However, when such an electrical contact is used for breaker requiring a higher duty, e.g., rated current of 10 A or more, a great breaking current flows through the contact, deteriorating properties called insulation properties. As a result, the electrical contact can be no longer used. This tendency can be seen also with an electromagnetic switch having a rated load of 35 AF or more. In some detail, the load current causes deterioration of insulation properties.

[0005]

Further, dispersion of properties of contact, e.g., low stability of solderability and consumption resistance,

particularly abnormally low soldering intensity and consumption resistance that often occur, is another problem with Cd-free contacts. This difficulty is one of the factors that limit the use of Cd-free contacts. For example, most of breakers having a rated current of 10 A or more and a breaking current of 1.5 KA or more still employ an electrical contact containing Cd in an amount of 10% by weight or more. On the other hand, electrical contacts made of Cd-free Ag alloy are normally used only for some light load magnet switches or relays.

[0006]

Under these circumstances, it has been desired to produce a contact having good insulation properties, little dispersion of properties and assured stability of solderability and consumption properties in particular at a reduced cost.

[0007]

[Problems that the Invention is to Solve]

In the light of these circumstances, an aim of the invention is to provide an electrical contact composed of a Cd-free Ag alloy raising no toxicity problem which exhibits good insulating properties, assured stability of solderability and consumption properties, a small probability of occurrence of abnormalities thereof and little dispersion thereof.

[0008]

[Means for Solving the Problems]

In order to accomplish the aforementioned aim, the electrical contact provided by the invention comprises an Ag alloy containing Sn in an amount of from 1 to 9% by weight and Cd as an impurity in an amount of less than 1% by weight and having an average hardness of 150 mHv or more on the microvickers scale defined in JIS at least on the surface thereof. The term "surface" as used herein is meant to indicate the contacting surface of two opening/closing electrical contacts.

[0009]

The electrical contact of the invention may have a two-layer structure comprising a surface layer having an average surface hardness of 150 mHv or more and a thickness of 10  $\mu\text{m}$  or more and an inner layer having a lower hardness than that of the surface layer. Further, the content of Sn in the surface layer is equal to or more than that of the inner layer.

[0010]

The electrical contact of the invention may comprise at least one element selected from the group consisting of In, Sb, Ca, Bi, Ni, Co, Zn, Te, Cr and Pb incorporated therein as additives other than Sn.

[0011]

In the electrical contact of the invention, the average hardness of the surface layer is preferably 160 mHv or more, more preferably 180 mHv or more, even more preferably 190 mHv or more. In the case where the average hardness of the surface layer is 220 mHv or more, an extremely excellent effect can be exerted.

[0012]

[Mode for Carrying Out the Invention]

The electrical contact of the invention is a Cd-free electrical contact composed of an Ag alloy comprising Sn in an amount of from 1 to 9% by weight and Cd, if incorporated as an unavoidable impurity, in an amount of less than 1% by weight. The reason for the limitation of Sn content to a range of from 1 to 9% by weight is that when Sn content is less than 1% by weight, the resulting electrical contact exhibits a raised dispersion of insulation properties and other properties and some deterioration in other properties which should be essentially provided for Cd-free contact, and when Sn content is more than 9% by weight, it is difficult to produce the desired contact. The content of Sn is preferably from 2 to 7% by weight. From the standpoint of absence of Cd, the content of Cd is preferably less than 0.01% by weight. Cd may be substantially absent.

[0013]

The electrical contact of the invention may comprise

at least one element selected from the group consisting of In, Sb, Ca, Bi, Ni, Co, Zn, Te, Cr and Pb incorporated therein in addition to Ag and Sn, which are essential components as mentioned above, for the purpose of improving various properties. In particular, when In is incorporated in an amount of from 1 to 9% by weight, the desired electrical contact can be easily produced. The content of In is preferably from 3 to 8% by weight. These elements such as Sn and In are normally dispersed in the Ag matrix particularly in the form of oxide, including elements described later.

[0014]

Referring to other additive components and their preferred content, Sb is incorporated in an amount of from 0.05 to 2% by weight, Ca is incorporated in an amount of from 0.03 to 0.3% by weight, Bi is incorporated in an amount of from 0.01 to 1% by weight, Ni is incorporated in an amount of from 0.02 to 1.5% by weight, Co is incorporated in an amount of from 0.02 to 0.5% by weight, Zn is incorporated in an amount of from 0.02 to 8.5% by weight, and Pb, Te and Cr are each incorporated in an amount of from 0.05 to 5% by weight. When the content of these elements, if any, fall outside the above defined range, the resulting electrical contact may exhibit deteriorated welding resistance and temperature properties depending on the kind of breaker. Further, when the content of these elements exceeds the upper limit of the above defined

range, the productivity of the electrical contact may be lowered depending on the kind of breaker.

[0015]

Even elements other than described above may be incorporated in a slight amount so far as it falls within the scope of the invention. As such elements there may be incorporated Ce, Li, Cr, Sr, Ti, Te, Mn,  $\text{AlF}_3$ ,  $\text{CrF}_3$  and  $\text{CaF}_2$  each in an amount of 5% or less, Ge and Ga each in an amount of 3% or less, Si in an amount of 0.5% or less and Fe and Mg each in an amount of 0.1% or less.

[0016]

The reason why the Cd-free electrical contact having the aforementioned chemical formulation has an average hardness of 150 mHv or more on the microvickers scale at least on the surface thereof is that when the average surface hardness falls below this level, the resulting electrical contact exhibits deteriorated insulation properties and raised dispersion of properties. Insulation properties are often properties that can be difficultly attained with Cd-based contacts. Cd-free contacts tend to have somewhat better insulation properties than Cd-based contacts but still leave something to be desired in insulation properties. In accordance with the invention, the limitation of the average surface hardness to 150 mHv or more makes it possible to solve the problems with the insulation properties of Cd-free

contacts. Further, Cd-free contacts often exhibit deteriorated consumption resistance that greatly prevents practical use thereof. This consumption resistance problem can be solved by raising the average surface hardness.

[0017]

In general, Cd-free contacts exhibit a great dispersion of material physical properties and thus cannot be processed under stable conditions at the bonding step, for example. Further, these Cd-free contacts don't exhibit a stable bond strength with respect to a base metal made of Cu or alloy thereof and thus are subject to separation from the Cu base in the field. In some cases, the dispersion of bond strength has caused dispersion of consumption resistance. Further, when the consumption resistance of Cd-free contact is deteriorated, the components of the contact are scattered to the environment by the load of large current, causing deterioration of insulation properties.

[0018]

The electrical contact of the invention has an average surface hardness of 150 mHv or more and hence stabilized physical properties leading to improvement as well as stabilization of the aforementioned bonding properties, etc. As a result, the properties of the electrical contact can be stabilized, making it difficult to generate abnormalities to advantage. Thus, in order to improve not only insulation

properties and consumption resistance but also bonding properties and other properties, the average surface hardness of the electrical contact is preferably as high as possible, more preferably 160 mHv or more, even more preferably 180 mHv or more, still even more preferably 190 mHv or more. In particular, when the average surface hardness of the electrical contact exceeds 220 mHv, there occurs substantially no dispersion. The measurement of Microvickers hardness is preferably effected at a load of 10 g or 25 g.

[0019]

The electrical contact of the invention suffices if it has an average surface hardness of 150 mHv or more. Accordingly, the entire electrical contact preferably has the same hardness. The surface hardness may have some distribution. In other words, there is a case where a site having a small content of dispersed components such as Sn, i.e., site having a low hardness occurs unintentionally on a part, e.g., center of the surface of the electrical contact. Even in this case, it suffices if the average surface hardness is 150 mHv or more. The term "average hardness" as used herein is meant to indicate an arithmetical mean of measurements of Microvickers hardness defined in JIS made on arbitrary points of the surface of the electrical contact. The number of measurement points is preferably 30 or more.

[0020]

A preferred embodiment of the invention is an electrical contact having a two-layer structure comprising a surface layer having an average hardness of 150 mHv or more and an inner layer having a lower hardness than that of the surface layer. In this embodiment, the thickness of the surface layer is preferably 10  $\mu\text{m}$  or more, more preferably from 20  $\mu\text{m}$  to 120  $\mu\text{m}$ . When the thickness of the surface layer falls below 10  $\mu\text{m}$ , it is difficult to improve the aforementioned properties. The surface layer having too great a thickness is disadvantageous in production cost. The term "thickness of surface layer" as used herein is meant to indicate an arithmetical mean of measurements of thickness of section of surface layer taken perpendicular to the surface of the electrical contact made on 5 points disposed parallel to the surface of the electrical contact using an optical microscope. The inner surface a commonly prepared Ag alloy having Sn oxide particles dispersed therein is 145 mHv at maximum.

[0021]

As a method of controlling the hardness of the surface layer and the inner layer there may be used a method involving the change of the chemical formulation of the two layers. For example, the content of Sn in the surface layer can be predetermined to be higher than that of the inner layer, making it assured that the hardness of the surface layer can

be higher than that of the inner layer. In the invention, however, the hardness of the surface layer may be higher than that of the inner layer while the chemical formulation of the surface layer and the inner layer are the same. The reason why the hardness level of the surface layer and the inner layer differ from each other while the two layers have the same chemical formulation is attributed to the fact that the microstructure of the two layers are each controlled properly. For the details of the hardness controlling method involving the controlling of microstructure, reference will be made in connection with a method of producing a contact described later. Of course, an electrical contact having a lower Sn concentration in the surface layer than in the inner layer as opposed to the present embodiment is included in the scope of the invention.

[0022]

Examples of the electrical contact made of materials different from surface to interior as in the electrical contact of the invention include those disclosed in JP-A-58-189913, JP-A-62-97213 and JP-A-61-114417. However, these related art electrical contacts are essentially different from the electrical contact of the invention in composite structure and effect and thus cannot attain improvements in properties intended by the invention.

[0023]

The electrical contact of the invention needs to be connected to other members such as base metal so that it can be incorporated in, e.g., a breaker depending on the purpose. In this case, in order to facilitate the bonding of the electrical contact to other members such as base metal, the electrical contact of the invention may have a thin connection layer made of a metal such as pure Ag and soldering material provided on the side thereof opposite the front surface. This connection layer may be in the same form as that of the metallic layer commonly provided for the same purpose. The bonding of the electrical contact to other members such as base metal is normally made via a connection layer as mentioned above. Alternatively, an Ag alloy which acts as an electrical contact may be directly formed on the base metal or may be formed integrally with the base metal.

[0024]

Figs. 1 to 3 each depict a representative example of the electrical contact having a surface layer and an inner layer according to the invention. The electrical contact of Fig. 1 is a typical example of the electrical contact comprising an inner layer 1 and a surface layer 2 formed only on the surface of the inner layer 1. A connection layer 3 is provided on the back side of the inner layer 1. The electrical contact of Fig. 2 comprises a surface layer 2 provided surrounding an inner layer 1 on the surface, back

surface and side surface thereof. The electrical contact of Fig. 3 comprises a surface layer 2 provided surrounding an inner layer 1 on the surface and side surface thereof. The electrical contacts of Figs. 2 and 3, too, comprise a connection layer 3 provided on the back surface thereof.

[0025]

A method of producing the electrical contact of the invention will be described hereinafter. The electrical contact having a hard surface of the invention can be prepared by powder metallurgy. For example, a particulate oxide made of Sn or In and other compounds or an Sn or In compound which can be heated to become oxides or new other compounds and an Ag powder are previously compounded and mixed at a predetermined proportion, and then optionally subjected to heat treatment. Similarly, a powder mixture having a chemical formulation, i.e., mixing proportion different from that mentioned above is prepared. Subsequently, the two powder mixtures are laminated, and then powder-molded to prepare a preform which is then sintered. As the post-sintering machining there may be applied any of various plastic processing methods such as hot extrusion, hot or cold rolling and hot forging. If necessary, rolling may be properly followed by heat treatment or shape adjusting step. The formulation and fineness of the raw material powder and the post-sintering machining and heat treatment conditions

can be properly devised to obtain an electrical contact having a hard surface layer, making it possible to control the properties of the electrical contact.

[0026]

Alternatively, using various metallurgical methods such as spray coating, thick film vacuum deposition (CVD, etc.), thick film printing, a surface layer may be formed on an inner layer of the electrical contact which has been prepared as a substrate by powder metallurgy or welding method. Further, a surface layer and an inner layer which have been separately prepared may be bonded to each other. The bonding of the two layers can be accomplished by any method such as diffusion bonding involving hot hydrostatic forming and hot extrusion. The laminate thus prepared may be further subjected to heat treatment so that the microstructure of the two layers can be intentionally controlled to attain respective desired hardness.

[0027]

In order to use melting method to produce an electrical contact of the invention, melting and casting are effected such that the desired chemical formulation of surface layer and inner layer can be attained. The ingots thus obtained are each then roughly rolled. The two rolled materials are then hot-pressed to make lamination. During or after this procedure, the aforementioned thin connection layer made of

pure Ag or the like is contact-bonded to the laminate as necessary. The laminate is further rolled to prepare a hoop having a predetermined thickness which is then punched (or further formed) to obtain an Ag alloy composite material having a size close to that of the final product. This Ag alloy composite material is then internally oxidized to convert the metallic components such as Sn and In to oxide. Dissolution/casting may be preceded by the incorporation of compounds other than oxide of constituent elements.

[0028]

As a method other than the aforementioned laminating method, there may be employed a method which comprises, even if one rolling material is used, providing a heat treatment step or shape adjusting step after rolling so that the microstructure can be intentionally controlled to raise the hardness of the surface layer or change the material properties or the level of the various layers. Another method involves as a part of the heat treatment step a step of keeping the material at an oxidizing temperature as low as about 600°C for 2 hours in the initial oxidizing stage followed by oxidizing at a temperature as high as 750°C. Of course, the material may be kept at the low temperature for a longer period of time, even until the termination of oxidation in some cases, to obtain a hard alloy.

[0029]

As a method of controlling the hardness of the electrical contact there may be used the following method besides the method mentioned above. In some detail, a method which comprises preparing a composite contact using the aforementioned method, and then rapidly heating and cooling only the surface layer of the composite contact so that the residual stress of the surface layer is greater than that of the inner layer or a method which comprises subjecting the surface layer to shot blasting to effect work hardening may be employed. Alternatively, a method may be used which comprises subjecting an Ag alloy sheet to heat treatment in addition to hot rolling and cold rolling, i.e., so-called thermomechanical processing (thermomechanical processing), and then subjecting the Ag alloy sheet to internal oxidation at a controlled temperature so that oxide particles which are finer than in the inner layer are separated out in the surface layer to raise the hardness of the surface.

[0030]

More alternatively, in the aforementioned method involving the lamination of the surface layer with the inner layer, optionally with the connection layer, by rolling, the surface layer and the inner layer may be predetermined to have the same chemical formulation but different forging ratios so that the two layers may have different hardness while having the same chemical formulation. The aforementioned

hardness controlling method can be effectively applied to the surface layer and the inner layer which have the same chemical formulation.

[0031]

[Example]

(Example 1)

Two Ag alloys having the chemical formulations as the surface layer and the inner layer set forth in Table 1 were individually melted and casted to prepare ingots.

These ingots were each roughly worked. The ingots for surface layer and inner layer were laminated on each other, and then bonded to each other at 850°C in an argon atmosphere over a heated roller to prepare a composite material composed of two layers of Ag alloy. The composite material thus obtained was preheated under the same conditions. A thin pure Ag plate was then hot contact-bonded to the composite material on the back side thereof opposite the front surface thereof to a final thickness of 1/10 of the total thickness to form a connection layer.

[0032]

Thereafter, the laminate was cold-rolled to obtain a hoop-shaped material which was then punched to prepare a composite contact tip of two shapes, i.e., shape A having a width of 7.5 mm, a length of 8 mm and a thickness of 2 mm and shape B having a width of 5 mm, a length of 5 mm and a thickness

of 1.5 mm. The various tips thus obtained were each then kept at 750°C in a 15 atm atmosphere for 210 hours to prepare various contacts as Samples 1 to 34 set forth in Table 1. The average hardness of the surface layer of the various sample contacts thus obtained on the microvickers scale and the thickness of the surface layer are set forth in Table 1 below. Although the hardness of the inner layer is not set forth in Table 1, the hardness of the inner layer is lower than that of the surface layer except Sample 27, which exhibits the same hardness in its entity, and Sample 33, which exhibits a higher hardness in the inner layer than in the surface layer.

[0033]

For the measurement of average hardness, the microvickers hardness was measured on a section along the direction perpendicular to the surface of the various sample contacts each at 5 points, including the upper and lower ends of the various layers in the thickness direction, in each region of the surface layer and the inner layer, and this job was conducted at 6 sites in the vicinity of the center of the sample. The arithmetic mean of these 30 measurements was then defined to be the average hardness of the various layers. By the way, in the case where the thickness of the surface layer was small, measurement was effected at 30 points in the direction parallel to the surface of the contact. Further, the thickness of the surface layer was measured at 5 points

in the direction parallel to the surface of the tip in the vicinity of the center of the same section, and the arithmetic mean of these 5 measurements was then defined to be the thickness of the surface layer.

[0034]

[Table 1]

Sample No.	Surface layer (wt-%)			Inner layer (wt-%)			Surface layer	
	Sn	In	Others	Sn	In	Others	Hardness (mHv)	Thickness ( $\mu$ m)
1*	0.8	0.9	-	1.2	1.2	-	140	40
2	1.5	1.2	-	1.0	1.2	-	150	40
3	2.4	2.2	-	2.2	2.1	-	165	40
4	2.9	8.0	-	2.2	2.1	-	173	50
5	9.0	3.1	-	8.6	2.1	-	270	50
6	3.4	3.4	-	3.2	3.1	-	185	50
7	5.0	5.0	-	4.4	5.0	-	193	50
8	7.0	5.0	-	6.0	5.0	-	224	50
9	8.0	5.0	-	7.8	5.0	-	305	50
10*	9.2	8.2	-	9.1	8.1	-	310	50
11	1.2	1.2	Sb	1.2	1.2	Sb	151	50
12	2.3	2.2	Sb	2.2	2.1	Sb	188	50
13	2.3	9.0	Sb	2.2	2.1	Sb	192	50
14	9.0	3.1	Sb	2.2	2.1	Sb	260	50
15	3.4	3.4	Ni	3.2	3.1	Ni	223	50
16	5.0	5.0	Ni	5.0	5.0	Ni	299	50
17	9.0	9.0	Bi	9.0	8.9	Bi	300	50
18*	9.2	9.2	Bi	9.0	9.1	Bi	320	50
19	5.0	5.0	Sb, etc.	5.0	5.0	Sb, etc.	300	8

20	5.0	5.0	Sb, etc.	5.0	5.0	Sb, etc.	287	11
21	5.0	5.0	Sb, etc.	5.0	5.0	Sb, etc.	286	26
22	5.0	5.0	Sb, etc.	5.0	5.0	Sb, etc.	286	32
23	5.0	5.0	Sb, etc.	5.0	5.0	Sb, etc.	286	70
24	5.0	5.0	Sb, etc.	5.0	5.0	Sb, etc.	286	118
25	5.0	5.0	Sb, etc.	5.0	5.0	Sb, etc.	286	360
26	5.0	5.0	Sb, etc.	5.0	5.0	Sb, etc.	286	950
27	5.0	5.0	Sb, etc.	5.0	5.0	Sb, etc.	286	Thickness of contact
28	5.0	5.0	Sb, etc.	5.0	5.0	Sb, etc.	303	50
29	5.0	5.0	Sb, etc.	5.0	5.0	Sb, etc.	315	50
30	2.0	3.0	Ni, etc.	2.0	3.0	Ni, etc.	170	50
31*	2.0	3.0	Ni, etc.	2.0	3.0	Ni, etc.	140	50

32	4.0	-	Ni, etc.	4.0	-	Ni, etc.	270	50
33*	1.8	-	-	7.8	-	-	140	50
34*	3.4	3.4	-	-	3.1	-	130	200

The symbol \* indicates comparative sample.

[0035]

In the formulation of the various samples set forth in Table 1, the amount of other components Sb, Ni and Bi in Samples 11 to 18 are each 0.2% by weight. Further, both the surface layer and the inner layer in Samples 19 to 32 have the same chemical formulation. Moreover, referring to other components in both the two layers in Samples 19 to 27 and their amount, the amount of Sb, Co and Zn are each 0.05% by weight and the amount of Ni is 0.2% by weight. Referring to other components in both the two layers in Sample 28 and their amount, the amount of Sb, Pb, Ni, Bi, Co and Zn are each 0.1% by weight and the amount of Ca is 0.2% by weight. Referring to other components in both the two layers in Sample 29 and their amount, the amount of Sb, Ni, Ca, bi, Co and Zn are each 0.1% by weight and the amount of Pb is 0.5% by weight. Further, referring to other components in Samples 30 to 32 and their amount, the amount of Ni and Zn are each 0.2% by weight.

[0036]

Samples 1 to 10 constitute a group of samples the Sn and In contents of which have been varied to control the

hardness of the various layers, Samples 11 to 18 constitute a group of samples the Sn and In contents of which have been varied and which have been further provided with other components, and Samples 19 to 27 constitute a group of samples the thickness of surface layer of which have been varied. Since Sample 27 has the same hardness throughout the contact, the thickness of the surface layer was represented by the thickness of contact. Further, Samples 19 to 30 constitute a group of samples the surface layer and the inner layer of which have the same chemical formulation and which, except Sample 27, have been prepared by raising the rolling ratio of the surface layer by 50% of that of the inner layer at the step of producing the surface layer and the inner layer and subjecting the material to annealing at a temperature as relatively low as 450°C for a period of time as short as 30 minutes in vacuo in the course of rolling and then subjected to shot blasting after oxidation for higher hardness to control the hardness of the surface layer. Sample 31 is an example of the sample having a hardness of less than 140 mHv and Sample 32 is an example of the sample free of In.

[0037]

Further, Sample 33 and Sample 34 are samples prepared according to the description in JP-A-61-114417 and JP-A-58-189913, respectively. In other words, the contact of Sample 33 is prepared by melting and casting various Ag

alloys of surface layer and inner layer having the formulations set forth in Table 1, subjecting the material to hot contact bonding/rolling, and then punching the material to prepare a contact which is then kept at 780°C in a 1 atm oxygen atmosphere for 210 hours to undergo oxidation treatment. The contact of Sample 34 is prepared by melting and casting various Ag alloys of surface layer and inner layer, forming a roughness having a 1 mm pitch and a 0.5 mm depth in the horizontal direction on the mating surface thereof, pressing the two layers at 2 ton/cm<sup>2</sup> while being heated to 400°C with the raised portion and fallen portion on the two layers engaged with each other so that they are hot contact-bonded to each other, cold-rolling the laminate, and then subjecting the laminate to oxidation treatment at 650°C in a 1 atm oxygen atmosphere.

[0038]

Subsequently, a fixed side base metal made of electrolytic copper and a movable side base metal made of electrolytic copper having shape as shown in Fig. 4 were prepared. The contact tip 5 having shape A and the contact tip 4 having shape B were then soldered to the fixed side base metal 7 and the movable side base metal 6, respectively. Thereafter, these base metals were fixed to an earth leakage breaker (hereinafter abbreviated as "breaker") having a rated AC 30-50A frame. Three units of such a breaker assembly were

prepared for each contact pair of the various samples. All the assemblies of Samples 1 to 34 were each then confirmed for insulating properties by a breaking test at a breaking current of 1.5 KA for 30 A frame or 5 KA for 50 A frame at a load of 220 V. For the insulating properties, the resistivity between the power supply loads was measured, and the lowest value is set forth in Table 2 below. Further, the consumed state of the original contact and the contact subjected to breaking test were compared with each other, and the consumed state of contact and its dispersion were then evaluated on the basis of 10 points.

[0039]

With respect to electromagnetic switch, too, the dispersion of consumed state of contact was similarly confirmed. In other words, electromagnetic switches rated as 400AF using the various contacts of Samples 1 to 34 were subjected to 4000A breaking test and closed at 2400A and opened at 400A 100,000 times. In the comparison between before and after the various tests, the degree of dispersion of contact consumption was visually confirmed, and the magnitude of dispersion of consumed state was evaluated on the basis of 10 points. Further, at the step of preparing the various samples, the adhesivity of the contact during the bonding the contact to the base metal was evaluated on the basis of 10 points by the state of solder flow, the presence

or absence of abnormalities such as crack on the surface of contact and the occurrence of bond trouble called bomb. The results of the aforementioned evaluations are set forth in Table 2 below.

[0040]

[Table 2]

Sample No.	Results of breaker test		Dispersion of consumption in electromagnetic switch test	Dispersion of adhesivity
	Insulation properties (MΩ)	Dispersion of consumption		
1*	0.4	1	2	4
2	2.7	5	5	7
3	16	6	6	8
4	25	7	7	8
5	80	9	8	9
6	71	8	8	8
7	∞	9	10	8
8	∞	9	10	9
9	70	8	7	7
10*	50	4	6	4
11	3.4	6	6	8
12	56	7	8	8
13	35	8	8	8
14	55	8	8	8
15	∞	9	8	8
16	∞	9	9	8
17	33	6	6	6
18*	16	4	5	3
19	58	5	7	5

20	59	7	7	7
21	68	8	8	7
22	69	8	8	7
23	80	8	8	7
24	87	8	8	8
25	90	8	8	9
26	$\infty$	8	8	10
27	$\infty$	9	8	9
28	80	7	7	7
29	80	8	9	7
30	18	7	6	8
31*	7.3	4	4	6
32	40	6	8	8
33*	0.4	5	4	4
34*	0.3	2	2	4

The symbol \* indicates comparative example.

[0041]

The aforementioned results show the following facts.

(1) The breakers and electromagnetic switches comprising contacts of the present invention having a surface layer Sn concentration controlled to a range of from 1 to 9% by weight, a microvickers hardness of 150 mHv or more on the average of the surface layer according to JIS, even preferably a surface layer thickness of 10  $\mu$ m or more fall within a range that can be sufficiently practically used according to the

aforementioned comprehensive evaluation. On the contrary, the breakers and electromagnetic switches comprising contacts of comparative examples deviating from the aforementioned range don't reach the practical level according to the comprehensive evaluation. (2) This applies also in the case where other components are incorporated in a small amount in addition to Sn and In. (3) Since the various contacts prepared on the basis of the description in JP-A- 61-114417 and JP-A-58-189913 were not subjected to any special hardness controlling treatment, the surface hardness level deviates from the range of the present invention, and neither of the two contacts could exhibit comprehensively practical level of performance.

[0042]

(Example 2)

Composite contacts having the same surface layer and inner layer chemical formulations as in Samples 3, 8 and 9 of Table 1 above were prepared. However, the inner layer was formed by the same casting/rolling method as used in Example 1 and the surface layer was formed by a vacuum plasma spraying method. In some detail, a rolling material made of an Ag alloy having the same chemical formulation as the inner layer was melted and casted in the same manner as in Example 1, a thin pure Ag connection layer was then hot contact-bonded to one side of the rolling material in the same manner as in Example

1, and the laminate was then rolled to a hoop form. These hoop materials thus obtained were each then punched to obtain a material having shape C having a width of 7.5 mm, a length of 8 mm and a thickness of about 2 mm and a material having shape D having length of 5 mm, a width of 5 mm and a thickness of about 1.5 mm which were then oxidized as in Example 1 to obtain an inner layer material.

[0043]

Thereafter, these materials were put in a vacuum chamber with the connection layer disposed at back side, and a surface layer was then formed on the front surface in the following manner. In some detail, an Ag alloy prealloy powder having the same chemical formulation as that of the surface layer of Samples 3, 8 and 9 above and a particle size distribution ranging from submicron to 2  $\mu$ m was prepared as raw material. Using argon gas as feed carrier gas, the prealloy powder thus prepared was sprayed and fixed onto the surface of the aforementioned inner layer material by a vacuum plasma spraying method to form a surface layer. By the way, during spraying, the forward end of the spray gun was automatically swung so that the surface layer thus sprayed becomes uniform. Further, in order to raise the adhesivity between the surface layer and the inner layer, the surface of the inner layer was previously exposed to plasma flame before spraying.

[0044]

The composite material thus obtained was then oxidized under the same conditions as in Example 1 to obtain contact tips of Samples 35 to 37. All the contact tips had a final surface layer thickness of 50  $\mu\text{m}$  and a pure Ag connection layer thickness of about 1/10 of the total thickness. The average hardness of the surface layer of the contact tips thus obtained was confirmed in the same manner as in Example 1. Further, the various contact tips were each mounted in the same type of breaker and electromagnetic switch as mentioned above in the same manner as in Example 1 and subjected to electrical test in the same manner as in Example 1. The results are set forth in Table 3 below.

[0045]

[Table 3]

Sample	Surface layer		Results of breaker test			Dispersion of consumption in electromagnetic switch test	Dispersion of adhesivity
	Hardness (mHv)	Thickness ( $\mu\text{m}$ )	Insulation properties ( $\text{M}\Omega$ )	Dispersion of consumption			
35	168	50	16	7	6	8	
36	290	50	$\infty$	8	10	8	
37	301	50	70	8	8	7	

[0046]

As can be seen in the aforementioned results, even the method which comprises forming a surface layer by a spraying method allows the production of a composite electrical contact comprising a surface layer and an inner layer having the same chemical formulation and having a surface layer average hardness of 150 mHv or more as in the casting method of Example 1 and the use of this contact makes it possible to provide a practically excellent breaker.

[0047]

(Example 3)

A composite electrical contact having the same chemical formulation of surface layer and inner layer as that of Samples 1, 2 and 6 of Table 1 above was prepared. However, the inner layer was formed by the same casting/rolling method as in Example 1, and the surface layer was then formed thereon by a vacuum evaporation method. In some detail, a rolling material made of an Ag alloy having the same chemical formulation as the inner layer was melted and casted in the same manner as in Example 1, a thin pure Ag connection layer was then hot contact-bonded to one side of the rolling material in the same manner as in Example 1, and the laminate was then rolled to a hoop form. These hoop materials thus obtained were each then punched to obtain a material having shape C and a material having shape D of Example 2 which were

then oxidized to prepare an inner layer material.

[0048]

Thereafter, these materials were put in a vacuum chamber with the pure Ag connection layer disposed at back side, and a surface layer was then formed on the front surface in the following manner. Firstly, a target having the same chemical formulation as that of the surface layer of Samples 1, 2 and 6 of Table 1 was prepared. Using the aforementioned target, these inner layer materials were each then subjected to vacuum metallization by a magnetron sputtering method while the temperature in the vacuum chamber was being kept at 180°C to prevent the reevaporation of Sn and the pressure in the vacuum chamber was being kept at an argon partial pressure of from few Torr to scores of Torr to form a surface layer having the same formulation as that of the target on the surface of the inner layer. By the way, in order to raise the adhesivity between the surface layer and the inner layer, the surface of the inner layer was previously cleaned with ion generated by high frequency before vacuum metallization.

[0049]

The various composite materials thus obtained were each then oxidized under the same conditions as in Example 1 to obtain contact tips of Samples 38 to 40. All the contact tips had a final surface layer thickness of 30  $\mu\text{m}$  and a pure Ag connection layer thickness of about 1/10 of the total

thickness. The average hardness of the surface layer of the contact tips thus obtained was confirmed in the same manner as in Example 1. Further, the various contact tips were each mounted in the same type of breaker and electromagnetic switch as used in Example 1 in the same manner as in Example 1 and subjected to electrical test in the same manner as in Example 1. The results are set forth in Table 4 below.

[0050]

[Table 4]

Sample	Surface layer		Results of breaker test			Dispersion of consumption in electromagnetic switch test	Dispersion of adhesivity
	Hardness (mHv)	Thickness (μm)	Insulation properties (MΩ)	Dispersion of consumption			
38*	143	30	0.4	2	1	3	
39	155	30	3.7	6	5	7	
40	187	30	80	8	8	8	

The symbol \* indicates comparative example.

[0051]

As can be seen in the aforementioned results, even the method which comprises forming a surface layer by a vacuum metallizing method allows the production of a composite electrical contact comprising a surface layer and an inner layer having the same chemical formulation and having a surface layer average hardness of 150 mHv or more as in the casting method of Example 1 and the use of this contact makes it possible to provide a practically excellent breaker.

[0052]

(Example 4)

Composite contact materials having the same chemical formulation as that of the inner layer of Samples 19 and 20 of Table 1 above were prepared by melting/casting, contact bonding of pure Ag connection layer and cold rolling method in the same manner as in Example 1. These materials were each put disposed in a shot blasting chamber with the surface layer upside, and only the surface was then selectively subjected to shot blasting with #120 alumina beads. Referring to the shot blasting conditions, unlike ordinary shot blast finish, shot blasting was effected at an ejection pressure as high as 6 kgf/cm<sup>2</sup> for 30 minutes.

[0053]

Thereafter, the composite contact materials were each then kept at 750°C for 210 hours in the same manner as in

Example 1 so that they underwent inner oxidation to obtain contact tips of Samples 41 and 42. The final combination of contact tips had the same size as that of Example 1, the thickness of the surface layer of all the samples was 20  $\mu\text{m}$ , and the thickness of the pure Ag layer was about 1/10 of the total thickness. The average hardness of the surface layer of the various contact tips was confirmed in the same manner as in Example 1. Further, the various contact tips were each mounted in the same type of breaker and electromagnetic switch as mentioned above in the same manner as in Example 1 and subjected to electrical test in the same manner as in Example 1. The results are set forth in Table 5 below.

[0054]

[Table 5]

Sample	Surface layer		Results of breaker test			Dispersion of consumption in electromagnetic switch test	Dispersion of adhesivity
	Hardness (mHv)	Thickness (μm)	Insulation properties (MΩ)	Dispersion of consumption			
41		20	50	5		5	5
42		20	57	7		7	7

[0055]

As can be seen in the aforementioned results, even the method which comprises forming a surface layer by a melting/casting method and then work-hardening the surface of the surface layer allows the production of a composite electrical contact comprising a surface layer and an inner layer having the same chemical formulation and having a surface layer average hardness of 150 mHv or more and the use of this contact makes it possible to provide a practically excellent breaker.

[0056]

(Example 5)

Composite electrical contacts having the same chemical formulation as that of surface layer and inner layer of Samples 1 to 4, 6, 7, 16, 21 and 25 to 27 of Table 1 above were prepared. However, the surface layer and the inner layer were separately prepared by a melting/casting method in the same manner as in Example 1, a surface layer material was subjected to cold high strength working at a percent draft of 50%, the two materials were hot contact-bonded to each other, a thin pure Ag layer was hot contact-bonded to the inner layer on the back side thereof, and the entire laminate was then rolled to obtain a hoop. This hoop was annealed at 300°C in vacuo of  $10^{-5}$  Torr or less for 2 hours, and then punched to two shapes having the same as in Example 1 to obtain

composite materials. The various composite materials thus obtained were each then oxidized in the same manner as in Example 1 to obtain contact tips of Samples 43 to 53.

[0057]

The size of the final combination of tips was the same as that of Example 1 and the thickness of the surface layer was predetermined to be the same as that of the various corresponding samples of Table 1 within  $\pm 2\%$ . The average hardness of the surface layer of the various samples thus obtained was only 10 to 20 mHv higher than the hardness of the corresponding various samples of Table 1. All the samples had a pure Ag connection layer thickness of about 1/10 of the total thickness. The various contact tips were each mounted in the same type of breaker and electromagnetic switch as mentioned above in the same manner as in Example 1 and subjected to electrical test in the same manner as in Example 1. The results are set forth in Table 6 below.

[0058]

Further, a sheet of melted and casted material having the same chemical formulation as that of Samples 43 to 53 above but a surface layer formulation was used rather than hot contact-bonding two sheets of melted and casted material, i.e., surface layer and inner layer, and this melted and casted material was hot contact-bonded to a thin pure Ag connection layer, and then subjected to oxidation at the same

step as mentioned above to prepare contact tips of Samples 54 to 64. However, oxidation was effected at 600°C in the initial stage of oxidation and then at 750°C. Further, referring to the thickness and average hardness of the surface layer, the oxidation temperature and oxidation time at lower temperatures were controlled such that the thickness and average hardness of the surface layer are the same as that of the corresponding various samples of Table 1 within  $\pm 2\%$ .  
[0059]

The various contact tips of Samples 43 to 64 thus obtained were each mounted in the same type of breaker and electromagnetic switch as mentioned above in the same manner as in Example 1 and subjected to electrical test in the same manner as in Example 1. The results are set forth in Table 6 below.

[0060]

[Table 6]

Sample No.	Dispersion of electromagnetic switch consumption		Dispersion of consumption in electromagnetic switch test	Dispersion of adhesivity
	Insulating properties (MΩ)	Dispersion of breaker consumption		
43*	0.4	2	3	4
44	3.7	5	5	7
45	16	6	6	8
46	29	7	7	8
47	88	8	8	8
48	∞	8	10	8
49	∞	9	9	8
50	74	9	9	7
51	98	8	8	9
52	∞	8	8	10
53	∞	9	8	9
54*	0.4	1	2	4
55	2.9	5	6	7
56	15	6	6	8
57	26	7	7	8
58	81	8	8	8
59	∞	9	10	8
60	∞	9	9	8

61	67	8	8	7
62	93	8	8	9
63	$\infty$	8	8	10
64	$\infty$	9	8	9

The symbol \* indicates comparative example.

[0061]

As can be seen in the aforementioned results, even the aforementioned method involving a melting/casting method allows the production of a composite electrical contact having an average hardness of 150 mHv or more and the use of this contact makes it possible to provide a practically excellent breaker.

[0062]

(Example 6)

Composite electrical contacts having the same chemical formulation of surface layer and inner layer as that of Samples 6 and 8 of Table 1 above were prepared. However, various materials having surface layer and inner layer formulations were melted and casted in the same manner as in Example 1, and then rolled to sheet. Subsequently, these sheet materials were laminated on each other, previously microwelded at the laminated portion to keep both the materials airtight, heated to 800°C in the atmosphere, and then hot-extruded at an extrusion ratio (sectional area ratio) of 80. A thin pure Ag connection layer was hot

contact-bonded to the inner layer of the composite material thus extruded on the back side thereof under the same conditions as in Example 1, and the laminate was rolled, and then punched to two shapes having the same size as that of Example 1. The composite materials thus obtained were each then subjected to internal oxidation in the same manner as in Example 1 to obtain contact tips of Samples 65 to 66.

[0063]

The final combination of contact tips had the same size as that of Example 1, the thickness of the surface layer of all the samples was 50  $\mu\text{m}$ , and the thickness of the pure Ag layer was about 1/10 of the total thickness. The average hardness of the surface layer of the various contact tips of Samples 65 to 66 was confirmed in the same manner as in Example 1. Further, the various contact tips were each mounted in the same type of breaker and electromagnetic switch as mentioned above in the same manner as in Example 1 and subjected to electrical test in the same manner as in Example 1. The results are set forth in Table 7 below.

[0064]

[Table 7]

Sample	Surface layer		Results of breaker test		Dispersion of consumption in electromagnetic switch test	Dispersion of adhesivity
	Hardness (mHv)	Thickness ( $\mu\text{m}$ )	Insulation properties of ( $\text{M}\Omega$ )	Dispersion of consumption		
65	198	50	76	8	8	8
66	299	50	$\infty$	9	10	8

[0065]

As can be seen in the aforementioned results, the lamination and subsequent hot extrusion/rolling of a surface layer and an inner layer prepared by a melting/ casting method allows the production of a composite electrical contact comprising a surface layer and an inner layer having the same chemical formulation and having a surface layer average hardness of 150 mHv or more as in Example 1 and the use of this contact makes it possible to provide a practically excellent breaker.

[0066]

(Example 7)

Composite electrical contacts having the same chemical formulation of surface layer and inner layer as that of Samples 8 and 15 of Table 1 above were prepared by powder metallurgy. In some detail, Ag alloy powders having the chemical formulation corresponding to these chemical formulations were each prepared and then subjected to internal oxidation in the same atmosphere and under the same conditions as in Example 1 in a rotary kiln. Thereafter, the various powders were laminated and molded in such a manner that the surface layer and the inner layer form the same combination of formulation as that of Samples 8 and 15 to prepare a columnar preform having a diameter of 80 mm and a total height of 200 mm. During this procedure, the portion

corresponding to the surface layer was predetermined to account for 1/10 of the entire combination.

[0067]

Subsequently, this preform was heated to 800°C in argon gas, and then immediately hot-extruded to sheet. A thin pure Ag connection layer was hot contact-bonded to the inner layer of the extruded material on the back side thereof in the same manner as in Example 1, and the laminate was rolled to obtain a hoop which was then punched to two shapes having the same size as that of Example 1 to obtain contact tips of Samples 67 to 68. The final combination of contact tips had the same size as that of Example 1 and the thickness of the pure Ag layer of all the samples was about 1/10 of the total thickness.

[0068]

The various contact tips of Samples 67 to 68 thus obtained were each confirmed for the average hardness of the surface layer and the thickness of the surface layer in the same manner as in Example 1. Further, the various contact tips were each mounted in the same type of breaker and electromagnetic switch as mentioned above in the same manner as in Example 1 and subjected to electrical test in the same manner as in Example 1. The results are set forth in Table 8 below.

[0069]

[Table 8]

Sample	Surface layer		Results of breaker test		Dispersion of consumption in electromagnetic switch test	Dispersion of adhesivity
	Hardness (mHv)	Thickness ( $\mu\text{m}$ )	Insulation properties ( $\text{M}\Omega$ )	Dispersion of consumption		
67	298	53	$\infty$	9	10	8
68	260	60	$\infty$	9	8	8

[0070]

As can be seen in the aforementioned results, even the composite contact prepared by powder metallurgy allows the production of a composite electrical contact having a surface layer average hardness of 150 mHv or more and the use of this contact makes it possible to provide a practically excellent breaker. All the aforementioned samples exhibited a Cd concentration of 0% by weight. In Samples 1, 4, 5 and 7, contacts having a Cd concentration of 0.01% by weight and 0.2% by weight were prepared. These contacts were each then evaluation in the same manner as mentioned above. All these contact samples showed little or no change of hardness and other properties. The change of these properties fall within the range of dispersion.

[0071]

[Advantage of the Invention]

In accordance with the present invention, a Cd-free electrical contact made of an Ag alloy containing Sn having improvements in insulation properties and its dispersion, which are weak points of related art Cd-free Ag alloy contacts, and hence excellent properties can be provided by controlling the average hardness of at least surface layer to 150 mHv or more, even preferably controlling the thickness of the surface layer to 10  $\mu$ m or more. Accordingly, the electrical contact of the present invention is free of Cd and thus can

be used in electrical apparatus such as breaker and electromagnetic switch in place of conventional electrical contact made of Ag alloy containing Cd.

[Brief Description of the Drawings]

[Fig. 1]

Fig. 1 is a schematic sectional view illustrating an embodiment of the electrical contact according to the invention.

[Fig. 2]

Fig. 2 is a schematic sectional view illustrating another embodiment of the electrical contact according to the invention.

[Fig. 3]

Fig. 3 is a schematic sectional view illustrating a further embodiment of the electrical contact according to the invention.

[Fig. 4]

Fig. 4 is a schematic perspective view illustrating an electrical contact of the invention mounted on a base metal wherein Fig. 4A indicates the movable side of the electrical contact and Fig. 4B indicates the fixed side of the electrical contact.

[Description of Reference Numerals and Signs]

- 1 Inner layer
- 2 Surface layer

- 3      Connection layer]
- 4, 5   Contact tip
- 6      Movable side base metal
- 7      Fixed side base metal

[Designation of Document]

Abstract

[Abstract]

[Problem] To provide an electrical contact composed of a Cd-free Ag alloy raising no toxicity problem which exhibits good insulating properties and assured stability of solderability and consumption resistance and can be applied to a breaker or high load electromagnetic switch.

[Means for Solution] An electrical contact comprising an Ag alloy containing Sn in an amount of from 1 to 9% by weight and Cd as an impurity in an amount of less than 1% by weight and having an average hardness of 150 mHv or more on the microvickers scale defined in JIS at least in the surface layer. Preferably, the electrical contact comprises a surface layer 2 having an average hardness of 150 mHv or more and an inner layer 1 having a lower hardness than that of the surface layer 2, wherein the thickness of the surface layer 2 is 10  $\mu\text{m}$  or more.

[Selected Drawing]

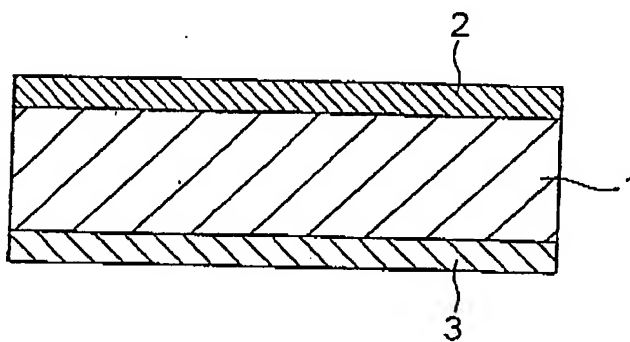
Fig. 1

【書類名】

図面

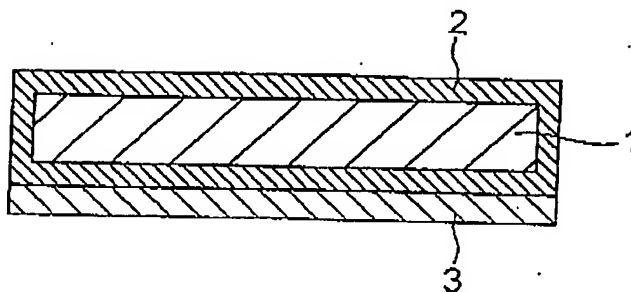
【図1】

Fig.1



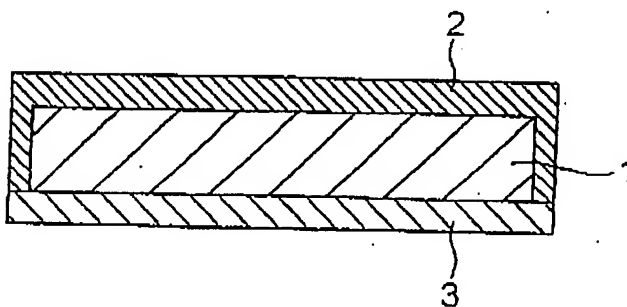
【図2】

Fig.2



【図3】

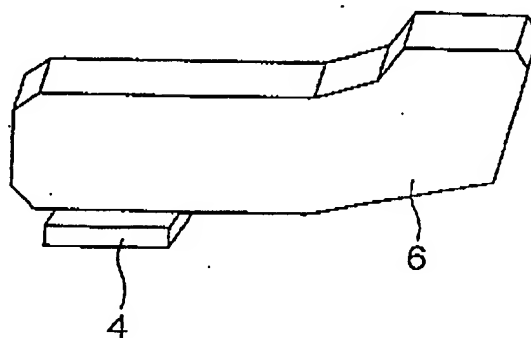
Fig.3



【図4】

Fig. 4

(a)



(b)

